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13 ABSTRACT

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CARBON FIBER STRUCTURE

This report describes studies of carbon fiber structure using optical and electron microscopy. Until recently most of the investigations of the fiber structure were directed toward determining the longitudinal orientation of the carbon and graphite crystallites. This study was concerned with the structure in cross section. A further knowledge of this structure is of importance in better understanding the mechanical properties of these fibers and determining means of controlling these properties.

The work reported herein was conducted in the period of November 1970 to July 1971 and was funded by the Naval Air Systems Command under Task A32 520/292/70 F 51-544-201. Portions of this report are taken from the Doctoral Thesis of the author submitted to the Chemical Engineering Department at the University of Maryland. The thesis work was directed by Professor Theodore G. Smith in conjunction with the staff of the Non-Metallic Materials Division at NOL.

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CONTENTS

ILLUSTRATIONS

INTRODUCTION

High-modulus, high-strength carbon fibers are produced by the pyrolysis of relatively inexpensive, commercially available polymeric textile fibers. Two precursor fibers which are most frequently used are cellulose (Rayon) and polyacrylonitrile (PAN). During the oxidation and pyrolysis of the polymeric fibers, a rearrangement of the carbon atoms into a near graphitic-like structure occurs. The purpose of this investigation was to determine the orientation of these crystallites in the fiber cross-section.

BACKGROUND

The moduli of carbon fibers are directly related to the size, perfection, and orientation of the crystallites in the fibers. The relationship of modulus to interlayer orientation is shown in Figure 1. For high-modulus fibers, small improvements in orientation can make large differences in the fiber modulus. A similar relationship does not exist between orientation and the fiber tensile strength. With unstretched fibers, the strength decreases as the orientation increases; while with fibers stretched during processing, the reverse is true in a linear fashion (30). Crystallite size has been measured for carbon fibers using x-ray techniques (13,23). Generally the size increases with increasing modulus. Since significant differences exist in the crystallite size and orientation in fibers made from different precursor materials, comparisons between these fiber types are difficult to make. Lower modulus fibers contain small crystallites with sizes ranging from 17 to 41 Å in the c-direction, while high-modulus fibers contain larger crystallites measured to be from 59 to 100 Å in the c-direction.

Measurements made on the interlayer spacings of crystallites in carbon fibers have been found to be around 3.41 to 3.47 Å (13,21). These values can be compared to values of 3.35 Å for natural graphite. The density of carbon fibers ranges from 1.5 to 2.0 gm./cm.^{3} while the density of natural graphite is 2.25 gm./cm.^{3} and that of pyrolytic graphite is 2.0-2.1 gm./cm.^{3} (38). It is, therefore, readily apparent that some carbon fiber structures may approach but are not equivalent to the structure of graphite. It has been suggested that interlayer spacings fall into two groups; those of 3.35 to 3.37 Å and those above 3.4 Å. This would indicate the existence of two phases; one

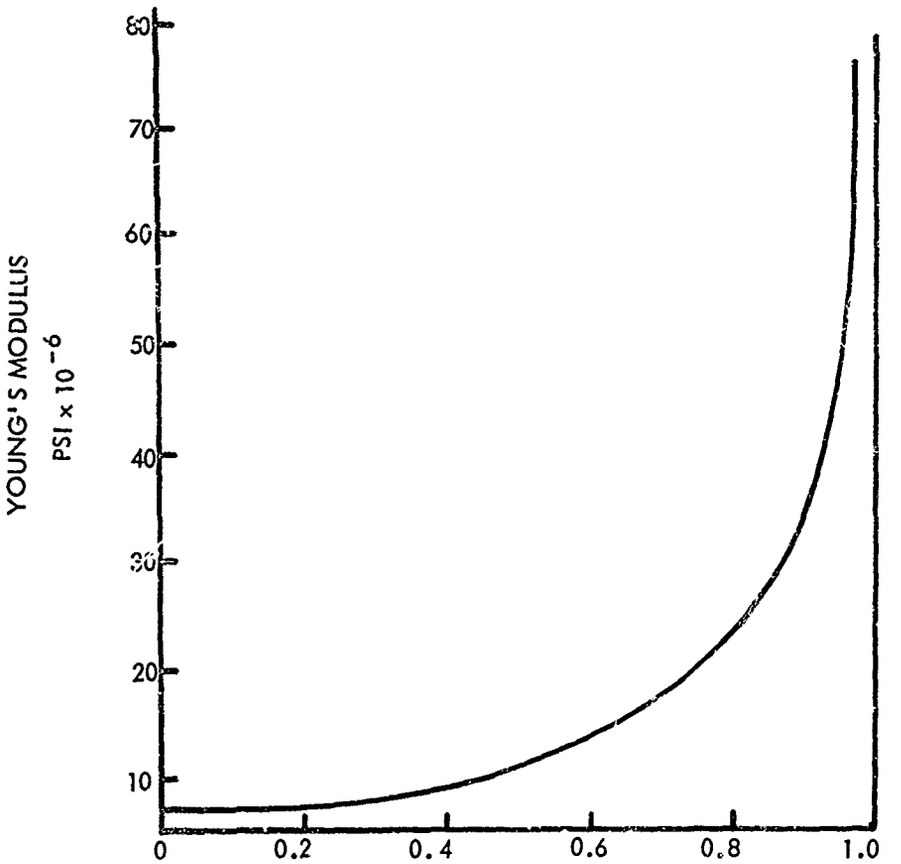


FIG. 1 RELATIONSHIP BETWEEN YOUNG'S MODULUS AND PREFERRED ORIENTATION, RAYON, PAN, AND PITCH-BASED FIBERS (23)

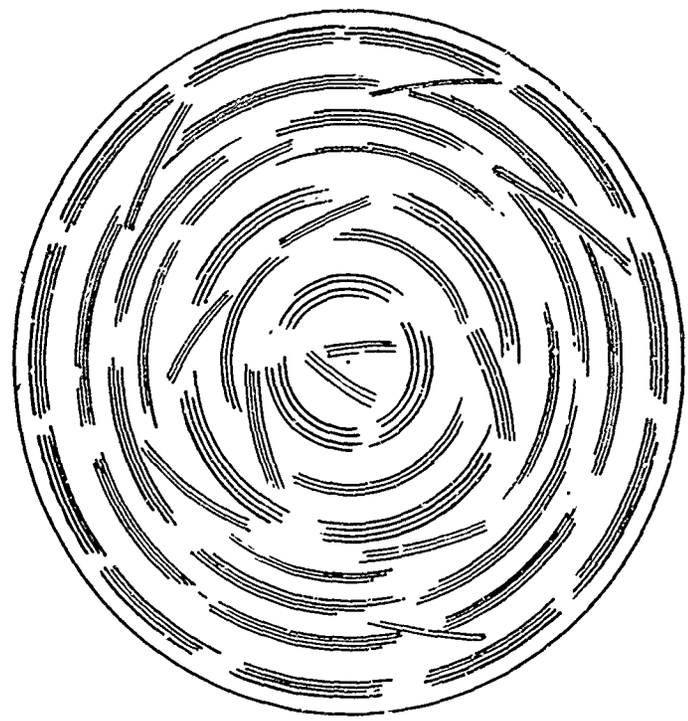


FIG. 2 CIRCUMFERENTIAL MODEL OF FIBER IN CROSS SECTION (9)

highly graphitic and axially oriented, and one non graphitic, probably turbostatic, and unoriented (21).

Bacon and Tang deduced from their early x-ray and microscopy studies of Rayon-based fibers that the crystallites were oriented axially in the fiber (6,54). Later work by Johnson, Watt, Badami, Joiner, and Jones showed the crystallites to be around 50 Å thick in the c-direction and grouped into bundles or fibrils about 1000 Å in diameter which run the length of the fibers (8,29). These fibrils are branched along the length of the fiber and have their basal planes parallel to the fiber axis.

An extensive study of crystallite orientation was presented by Butler in 1969 in a thesis on carbon fiber microstructure (13). His work concluded that carbon fibers are themselves composites composed of graphite crystallites and organized carbon. The crystallites at the surface of the fibers are larger and more graphitic. Their spatial orientation is not only parallel to the fiber axis, but also parallel to the fiber surface. The fiber structure deduced by Butler from polarized light microscopy of fibers derived from round PAN precursors is termed the circumferential model and is diagrammed in cross section in Figure 2. The low interlaminar shear strengths achieved in composites was related to this fiber microstructure. Butler attributes shear failures to interlayer failures within the outer layers of the fibers themselves rather than in the matrix or at the fiber-matrix interface.

Recently several microscopists have published high magnification micrographs (up to 5 million X) of longitudinal sections showing the axial alignment of the crystallites with the 3.4 Å layer spacings resolved (26,31). Harling has also published a few micrographs of transverse fiber sections (27). One such micrograph of a small portion of a fiber cross-section showed a very random crystallite arrangement. At the high magnification the area viewed was extremely small and the portion of the cross-section was not identified. One prevalent current opinion, however, is that the crystallites are randomly oriented in the fiber cross-section with perhaps some short-range order (23). A few other investigators have alluded to more highly-developed cross-sectional order.

EXPERIMENTAL WORK

Most of the work to date in carbon fiber structure analysis has been done using x-ray diffraction. While more work certainly could be done using this technique, it was not included in this study. Instead three microscopic methods were used: light microscopy, transmission microscopy, and electron scanning microscopy.

A. Light Microscopy

Polarized light microscopy is a standard crystallographic method for determining crystallite orientation in anisotropic materials. An isotropic material will appear dark regardless of its orientation with respect to the polarizer or analyzer. In this type of work the polarizer and analyzer are oriented perpendicular to each other.

An optically anisotropic material appears dark (extinction) when its optic axis is parallel to either the polarizer or analyzer and appears light when the optic axis is at other orientations (34). Extinction occurs at every 90° rotation thus indicating the order within the material. Additional information can be obtained through the use of a sensitive tint plate. A colorless mineral (such as gypsum), cut to a thickness as to produce violet interference color, is inserted between the objective and analyzer. Orientations at which extinction occurs appear violet. Other orientations cause either reinforcement of the light rays giving blue or opposition in the light rays producing red (56). The red and blue occur at orientations perpendicular to each other and at 45° from extinction.

Graphite is optically anisotropic when viewed perpendicular to its basal planes (c axis). Carbon fibers, when viewed in cross-section, are so oriented. The individual crystallites cannot be resolved but basic patterns in orientation and long-range order within the fiber can be determined. In preparing carbon fibers for viewing, the fibers were first fabricated into unidirectional composites with epoxy resin as the matrix. The composites were then sectioned, mounted in Bakelite with one end exposed, and polished. Care was taken during polishing so that the resin was not preferentially removed leaving the fiber ends in relief. Polished specimens which were not perfectly smooth did not exhibit the extinction patterns and required further polishing. The polishing sequence was as follows:

#100 to #600 silicon carbide paper
#95 optical finishing powder
1 micron alumina or cerium oxide
0.3 micron alumina (Linde A)
0.1 micron alumina (Gamma)

The polishing papers and the aluminas were used in conjunction with a distilled water-dilute soap solution. For the final polishing with the Linde A and Gamma powders, a Syntron vibratory polisher was used. Long duration vibratory polish (up to 24 hours) was necessary to avoid smeared graphite around the fiber edges. The polished sections were then viewed and photographed in a Bausch and Lomb Metallograph at 500 x and 1000 x under polarized light illumination and sensitive tint.

B. Transmission Microscopy

Transmission microscopy was used to examine the surfaces of treated fibers and to study the fiber strucutre. For the surface examinations, replication techniques using cellulose acetate, evaporated chromium, and evaporated carbon were employed (13). Structural determinations were made using thin sections from which adequate resolution could be obtained to study the cross-section crystallite orientation on a microscale. Thin sectioning of carbon fibers was first attempted by Bacon (6). He noted that the fiber cross-sections would crack parallel to the edge of the blade as it cut through the fiber. This is due to the high angle (45°) between the block face being cut and the section being removed. To prepare fibers for thin sectioning, small buhdles of fibers (about 1000 filaments) were mounted in ERLB 4617 epoxy resin. This was the resin of choice because of its hardness and good bonding characteristics with the fibers. Thin sections approximately 700 Å thick (silver sections) were made using a diamond knife and an LKB ultramicrotome. The sections were floated onto a 100 mesh grid covered with a formvar film. In early attempts it was discovered that the fiber sections would fall out of the surrounding epoxy section if not supported by the film. The fiber sections supported by the film were cracked as Bacon had experienced but were complete enough for viewing of many areas. At high magnifications, though, the graininess of the film obscured the layer resolution. Next, films were prepared having many small holes. Blowing on the formvar film before drying causes water vapor to condense and produces a holey film (44). Portions of fiber sections supported by such films then would be situated over holes which would permit unobstructed viewing. The sections were viewed and photographed at JOEL, LTD., Medford, Massachusetts, on a JEM-100B electron microscope.

C. Etching

A third method which gave some indication of fiber structure was the plasma etching of fiber cross-sections in composites. The fiber ends in an epoxy matrix were exposed to oxygen at a reduced pressure (0.15 torr) in the presence of an electrodeless discharge (frequency: 100 megahertz, potential: 330 volts, discharge current: 170 milliamps). The method has been described by Goan for oxidizing fiber surfaces (24) and was adapted to fiber morphology studies by Norr (43). Longer exposures of about 8 hours were required to achieve sufficient oxidation to reveal the structural details within the fibers. The fiber ends were then viewed in an Ultrascan SM-2 scanning electron microscope.

RESULTS AND DISCUSSION

Fiber structure considerations were made from observations on a macro scale (light microscopy) and observations on a micro scale (transmission microscopy). The macro observations revealed the gross or general orientation and structure of the fibrils or groups of crystallites within the fiber. The micro observations revealed the alignment of the individual layer planes (3.4 Å spacings) within the crystallites. Both types of observations are necessary to enable the construction of a model of the fiber structure.

A. Macro Orientation

Macro observations were made on PAN-based and Rayon-based fibers of intermediate and high modulus. The orientation differences in fibers made from these two types of precursors were significant while the differences between intermediate and high-modulus fibers from the same precursor type were slight and not in the orientation of crystallites within the fibers but in the degree of development of the crystallites. More highly developed crystallites are formed at the higher temperature stress graphitizations.

1. PAN-Based Fibers

Polarized light micrographs of PAN-based fibers having round cross-sections showed that the fibers treated to the highest graphitizing temperatures (high-modulus fibers) had the same extinction patterns as intermediate-modulus fibers). The polarized light pattern shown in Figure 3a is typical of both high-modulus and intermediate-modulus fibers from British manufacturers. This pattern has been called the 4-dot pattern and has been observed by other investigators (13,33). Round cross-section PAN-based fibers of other manufacturers do not always show the same pattern. Figure 3b is a polarized-light micrograph of fibers for which a maltese extinction cross is observed. The pattern formation is indicative of the fiber structure but is not a function of the end fiber product (fibers showing either pattern type can have high or intermediate tensile strengths and moduli). The type of pattern (i.e., the cross-section orientation of the fiber) is determined by the fiber processing. The major difference in the two fibers shown in Figure 3 is the duration of the low-temperature oxidation step (33). The structure that is developed during the subsequent fiber processing is strongly influenced due to a memory of the structure development during the oxidation. The 4-dot pattern is the result of shorter oxidation times while the maltese cross is the product of longer or complete oxidation. It was observed that when fiber diameters varied within a bundle, both types of patterns could be observed with the smaller diameter fibers displaying the maltese cross and the larger diameter fibers exhibiting the 4-dot center. This indicates that the

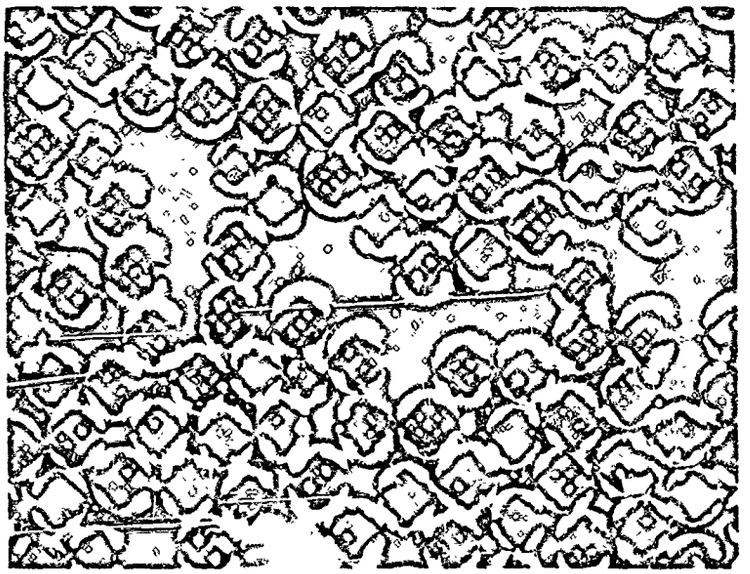


FIGURE 3a. POLARIZED LIGHT MICROGRAPH OF HIGH-MODULUS PAN-BASED FIBERS (Partial Low-Temperature Oxidation)

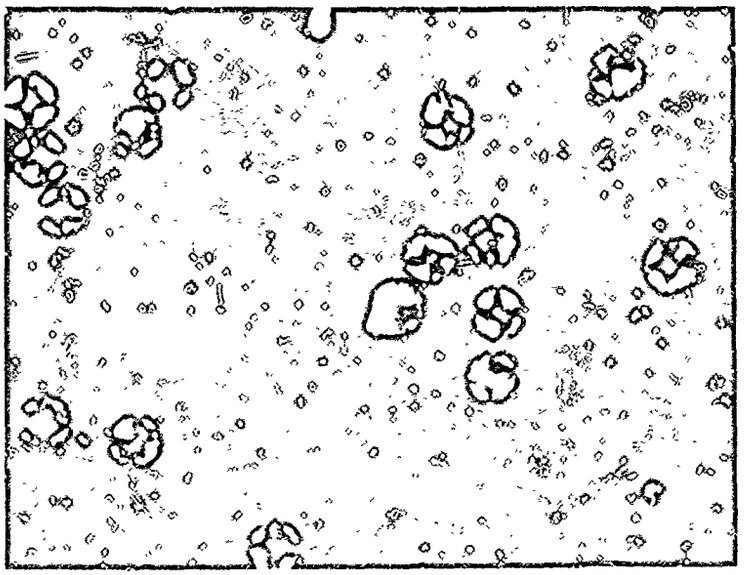


FIGURE 3b. POLARIZED LIGHT MICROGRAPH OF HIGH-MODULUS PAN-BASED FIBERS (Complete Low-Temperature Oxidation)

organization of crystallites proceeds from the outside of the fiber towards the center and is time dependent. The low-temperature oxidation step is, therefore, diffusion controlled.

Conclusions as to the significance of the two types of patterns seen in the polarized-light micrographs are difficult to make. The indication is that orientation exists on a gross scale within the fiber. Also there must be some radial uniformity in the orientation because the extinctions occurred at any orientation of the specimen with respect to the polarizer or analyzer. Two types of orientations, one like the spokes of a wheel and the other like the rings of a tree, would give rise to these types of extinctions; but neither would explain the 4 dots in the center of the pattern shown in Figure 3a. The use of sensitive tint helps to solve the problem. When pyrolytic graphite is photographed under sensitive tint and the layer planes are rotated $\pm 45^{\circ}$ from extinction, a color change from blue to red occurs. Orientations at extinction appear violet. The maltese cross pattern under sensitive tint shows red and blue segments perpendicular to each other indicating a 90° change in the crystallite orientation (Figure 3b). Using pyrolytic graphite with its known layer orientation, the orientation of the layers near the outside of the fiber was found to be parallel to the surface or circumferentially arranged forming a pattern like the rings of a tree (Figure 2). The same orientation continues into the center of the fibers thus forming the patterns which appear like the slices of a pie.

The 4-dot pattern under sensitive tint reveals a change of color at the outer perimeter of the fiber in each quadrant but also another change between the outer ring of the fiber and the interior. The dots in opposite quadrants and the outer ring segments in opposite quadrants are the same color (either blue or red). However, the dot in any quadrant is not the same color as the outer ring segment in that same quadrant. This indicates an orientation change between the outside and inside of the fiber. From the pyrolytic graphite, the orientation of the outside ring was determined to be circumferential, the same as with fibers exhibiting the maltese extinction cross. The same orientation, however, does not continue into the center of the fiber. The change in color necessitates that the center portion of the fiber be radially oriented like the spokes of a wheel. The model devised to represent this structure is termed the radial-circumferential model and is diagrammed in Figure 4. Such a model reflects to a degree an orientation within the precursor fiber which may be radial and which changes orientation due to the growth direction of the carbon (or graphite) crystallites as the precursor fiber is processed. Complete first-step low-temperature oxidation results in complete circumferential orientation. Less oxidation results in a fiber structure which is partially circumferentially oriented (outside) and partially radially

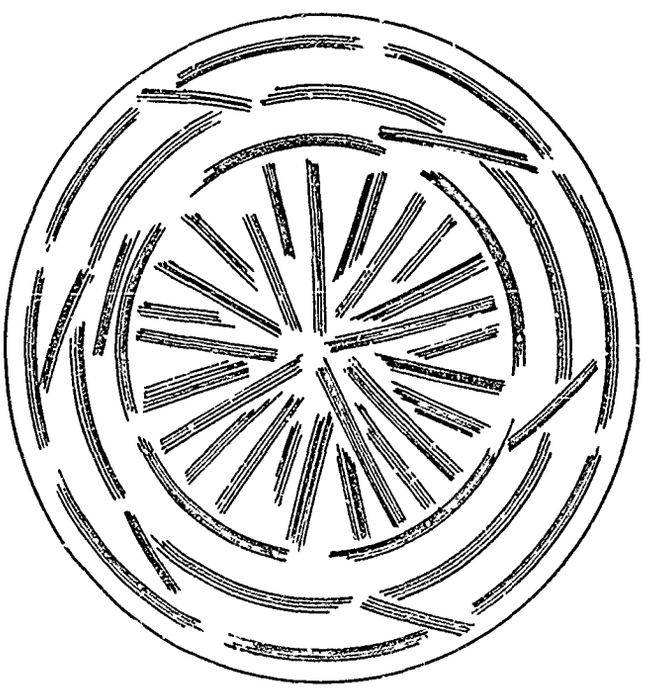


FIG. 4 RADIAL-CIRCUMFERENTIAL MODEL OF A PAN-BASED CARBON FIBER CROSS SECTION

oriented (inside). Complete oxidation is not essential in the formation of high-quality fibers as is indicated by the British fiber properties. Less than complete oxidation is understandable when the long oxidation times to achieve complete oxidation through the slow diffusion process are considered.

An axial cut through the diameter of a fiber oriented in the radial-circumferential manner should yield edge plane exposures near the outside of the fiber and basal plane exposures near the center (Figure 5a). Under polarized light, edge planes are optically active and basal planes are inactive. The radial-circumferential structure is confirmed by polarized-light micrographs of unidirectional composites with axially polished faces (Figure 5b). The basal-plane extinctions (due to the optical isotropy of the basal planes) are seen in those fibers which are cut very near the center. As the cut moves away from the center, due to the waviness of the fiber in the composite, the extinctions become narrower and disappear.

Further evidence of a radial-circumferential structure can be seen in fibers which have been plasma etched end-on with severe exposure to the oxidative environment. It is believed that this type of oxidation is partially selective and attacks carbon more readily than graphite. The structure of the more highly graphitic high-modulus fibers after such oxidation can be seen in the SEM micrograph shown in Figure 6. The radial inside structure with the circumferential rim on the outside can be observed. This approach to fiber structure determinations is not conclusive in itself but when coupled with the other information makes a more complete picture.

Other PAN-based fibers having dog-bone cross-sections instead of the usual round sections were examined under polarized light and sensitive tint. These fibers did not reveal the same organized structure in cross-section but showed rather weak polarized light patterns similar to those of low-modulus irregular-cross-section Thornel fibers. Under sensitive tint, the dog-bone cross-section fibers exhibited very small areas of red and blue coloring randomly spaced throughout the cross-section. These small spots could be seen in the microscope but were not easily photographed. The random-spot patterns indicate short-range but no overall or long-range orientation in the fiber cross-section.

2. Rayon-Based Fibers

Polarized light patterns obtained on Thornel 40 and Thornel 75 fibers showed a much different orientation than the round cross-section PAN-based fibers. Thornel 40 fibers exhibited weak patterns with intensity only at the perimeter (Figure 7a). This indicates that well-developed

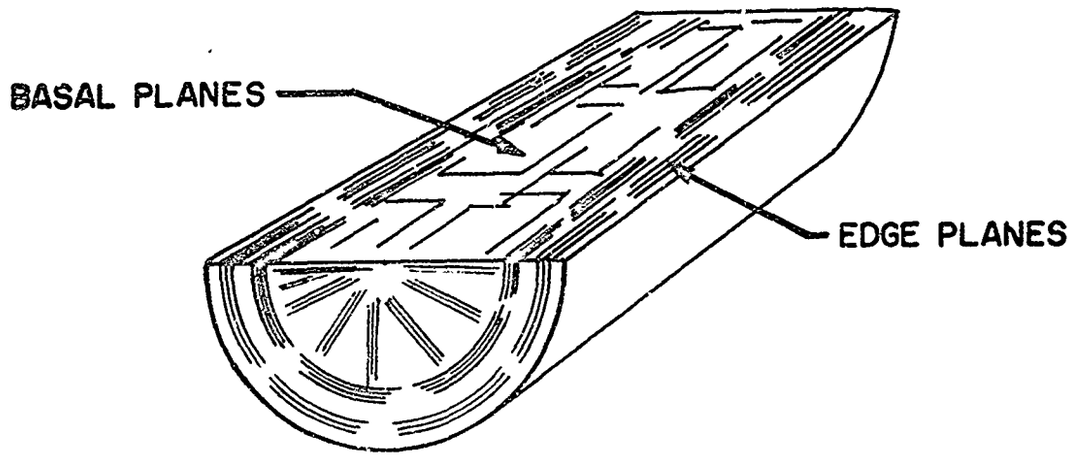


FIGURE 5a. AXIAL CENTER SECTION OF A FIBER SHOWING EDGE PLANE AND BASAL PLANE EXPOSURES

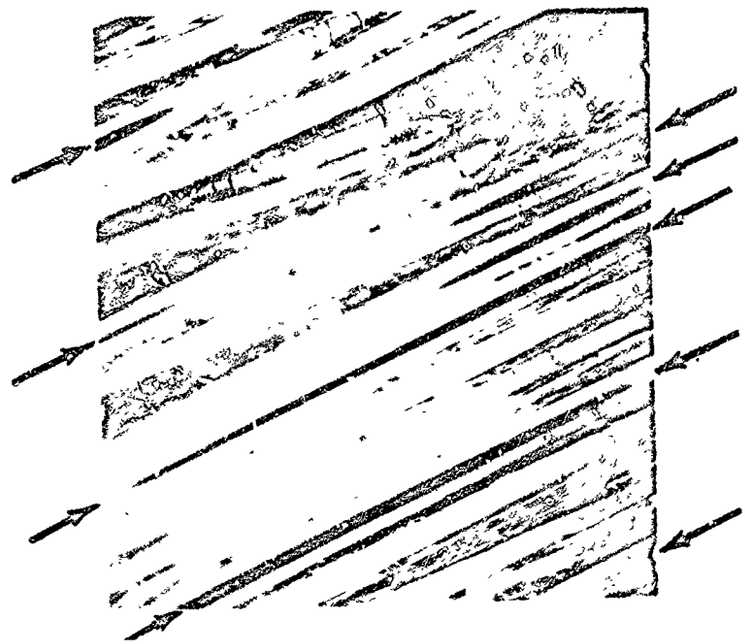


FIGURE 5b. POLARIZED-LIGHT MICROGRAPH OF A UNIDIRECTIONAL COMPOSITE SHOWING EXTINCTION BANDS IN THE CENTERS OF FIBERS

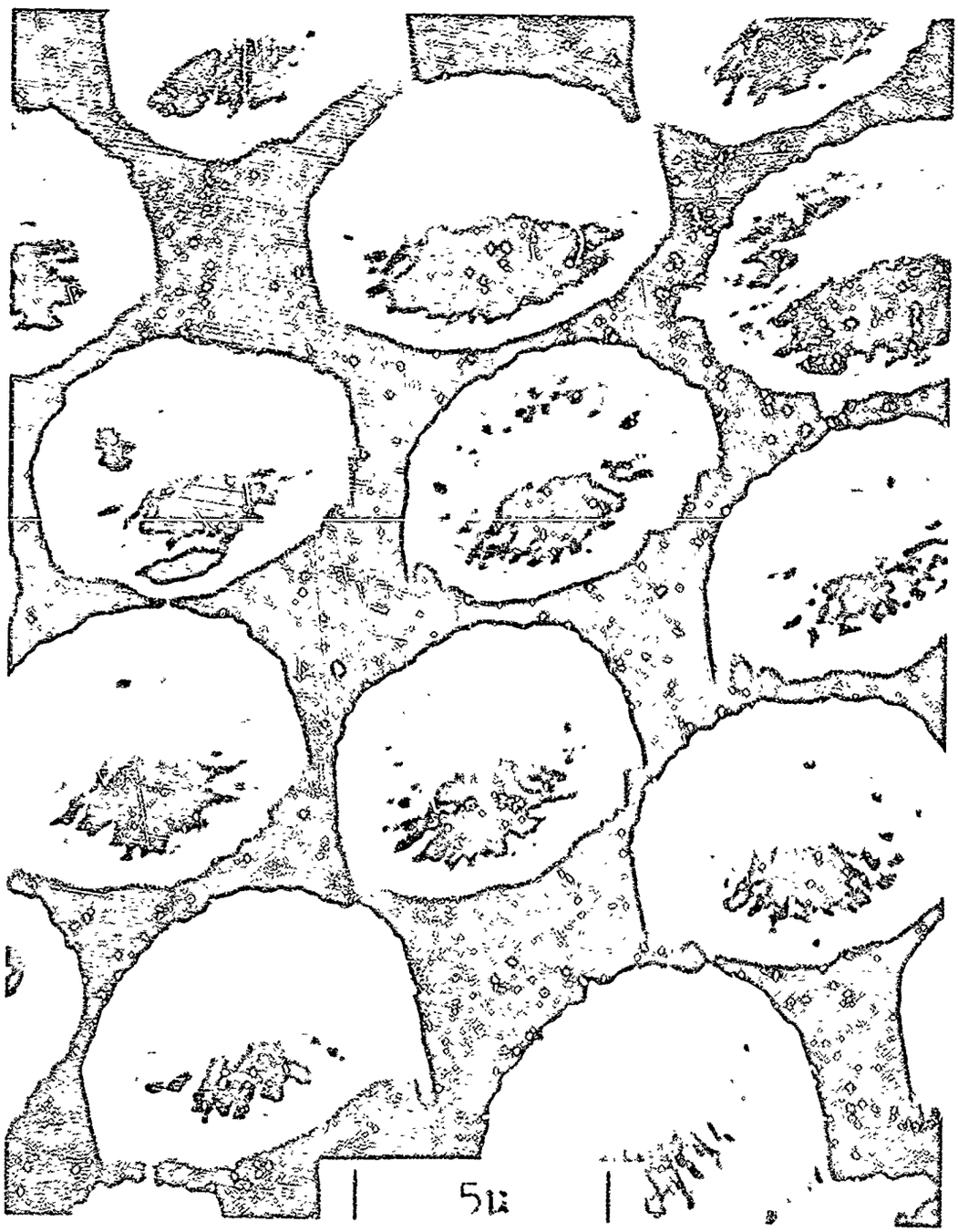
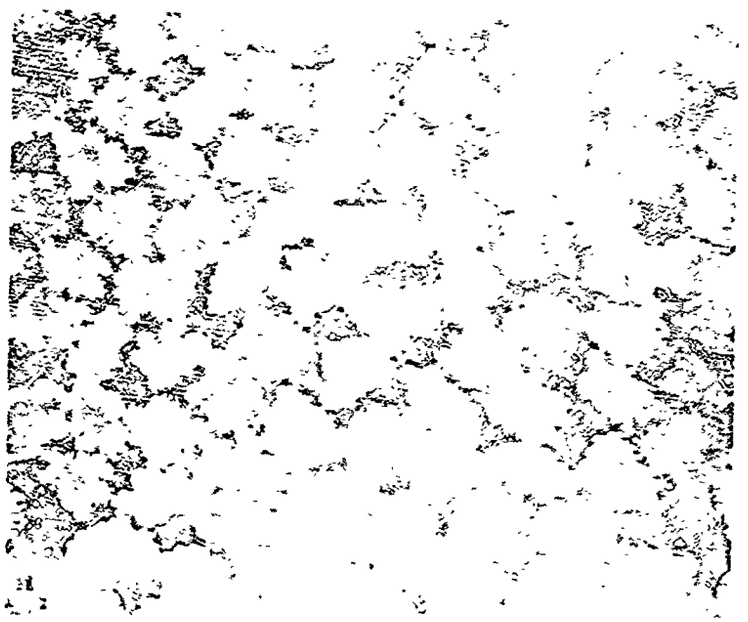
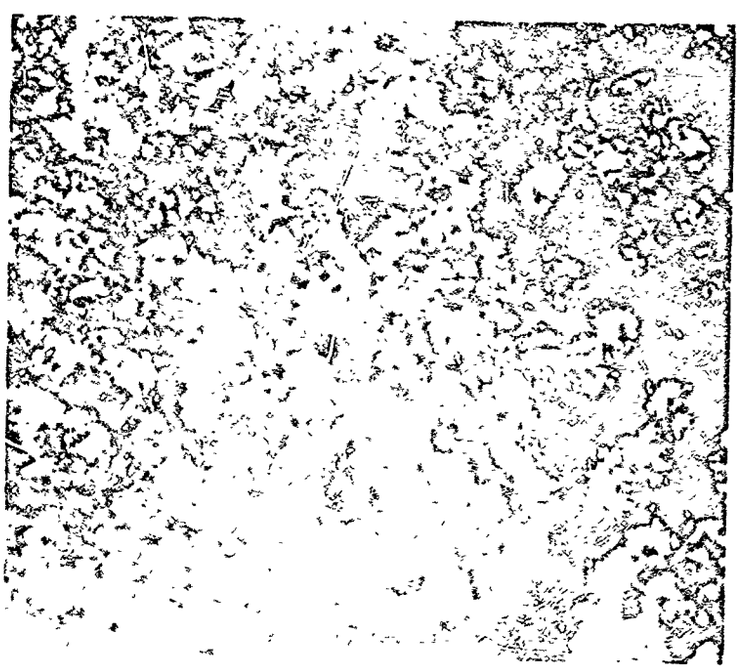


FIGURE 6. SEM MICROGRAPH OF HIGH-MODULUS FIBERS, RF PLASMA OXIDIZED, SHOWING RADIAL - CIRCUMFERENTIAL CRACKS



a. Thornel 40



b. Thornel 75

FIGURE 7. POLARIZED LIGHT MICROGRAPHS OF THORNEL FIBERS

crystallites are present only near the surface of this intermediate-modulus fiber. Thornel 75, on the other hand, exhibited strong extinction patterns which extended into the centers of the fibers (Figure 7b). This is significantly different than for the PAN-based fibers where both intermediate and high-modulus fibers exhibited the same patterns. In the Thornel fibers, the patterns show there is order within the fibers; especially within the lobes on the outside. They are not symmetrical due to the irregular perimeter of the fibers and the unsymmetrical radial orientation of the lobes. The patterns can be radically changed by rotation of the specimen. Thornel fibers, therefore, do not have the rotational symmetry present in the round PAN-based fibers.

Sensitive tint micrographs revealed the orientation to be parallel to the fiber surface. In the Thornel 40 fibers, this structure is well-developed only near the surface. Nearer the center of the fibers, the orientation may be similar or perhaps more random; but in any case, the crystallites are not as well developed. In the Thornel 75 fibers, the color patterns extend well into the centers of the fibers. Again the color change from red to blue represents an orientation change of 90°. The color changes occur primarily with changes in the irregular perimeter of the fiber. From analysis of the color patterns, it can be seen that the orientation in the lobes of the fiber follows the surface contour and extends into the center of the fiber. In several fibers where defects exist, the color patterns are much stronger indicating an even greater crystallinity in these fibers..

A model of the structure of Thornel 40 and Thornel 75 fibers is shown in Figure 8. The well-developed perimeter structure and more random less-developed center of the Thornel 40 fiber is contrasted with the more highly crystalline well-developed structure in the Thornel 75 fiber.

B. Micro Orientation

Thin transverse sections of high-modulus fibers cut with a diamond knife are shown at low magnification (4000 X) in Figure 9a. The cracks in the fiber section are due to the high angle of departure, (45°), the section must make when cut from the block face and are impossible to eliminate. Portions of the fiber sections remained bonded to the resin matrix and, therefore, remained in the same orientation as in the fiber. Those sections in the centers of the sections which were not connected to the resin matrix could be viewed, but the orientation may have shifted from what it originally was in the fiber. The sections were supported on 200 mesh grids covered with holey films which prevented the broken fiber sections from falling out of the epoxy matrix. At the high magnifications necessary to resolve the structure, viewing had to be done in the unobstructed areas where holes

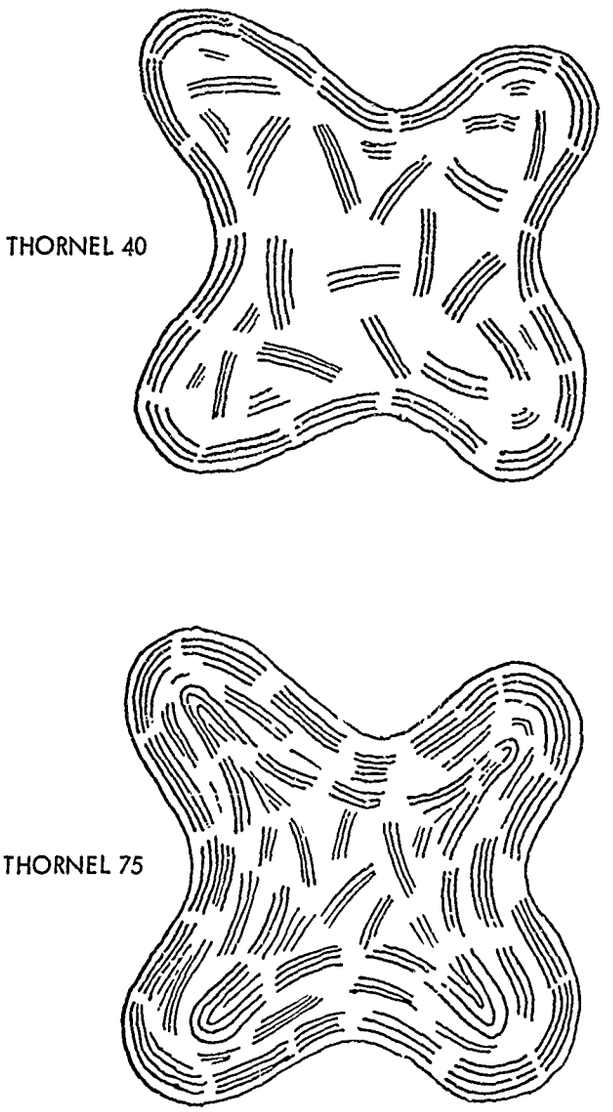


FIG. 8 MODEL OF INTERMEDIATE AND HIGH MODULUS THORNEL FIBERS

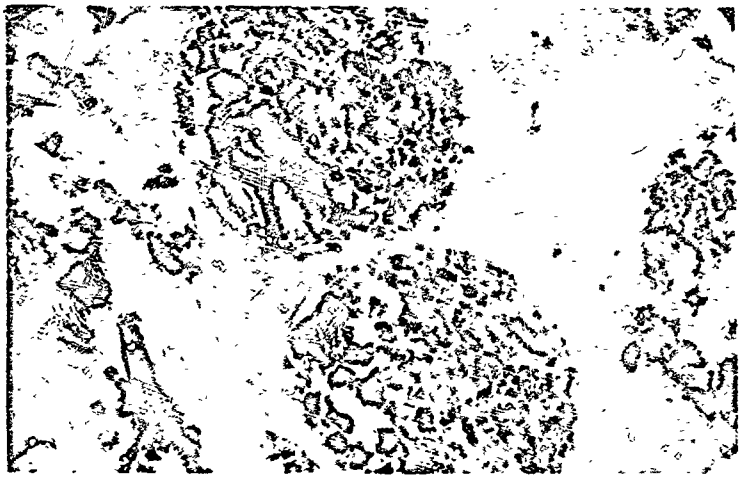


FIGURE 9a. FIBER THIN SECTIONS SHOWING CRACKS MADE DURING SECTIONING

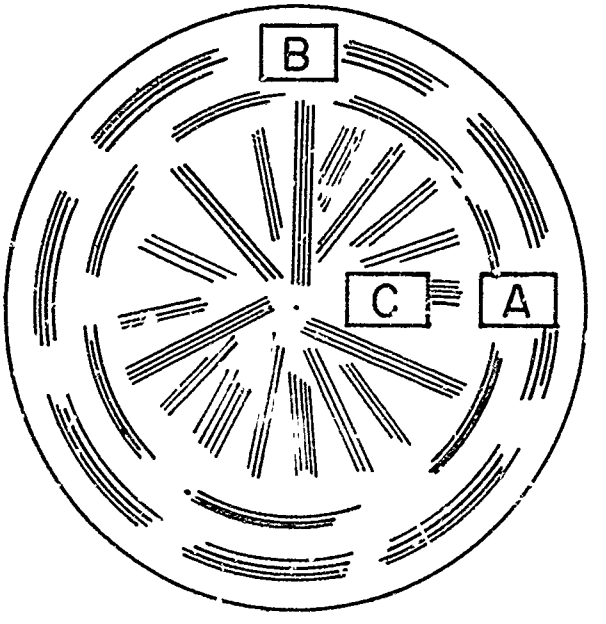


FIGURE 9b. ORIENTATION OF AREAS VIEWED AT HIGH MAGNIFICATIONS

occurred in the support film. Viewing was done in three areas designated A, B, and C in Figure 9b. Orientations could not be determined in areas marked C because no sections could be found which were still attached to the matrix. Figures 10a and b show areas A and B respectively in a high-modulus PAN fiber. The order in the crystallites can be seen and the 90° shift in orientation b between areas A and B is apparent. Figure 10c shows the structure in a Thornel 75 fiber as being ordered and parallel to the fiber surface. Figure 10d shows the structure in an area A of an intermediate-modulus PAN-based fiber. This can be compared with the high-modulus PAN-based fiber. The crystallites are oriented but not as highly developed or as large as in the higher-modulus fiber. The number of layer planes which can be observed in a single crystallite is around five or six. In the higher-modulus fibers, larger and more well-developed crystallites containing 10 to 50 layer planes can be observed. These micrographs confirm the structural orientation in the fibers as being parallel to the fiber surface, thus forming a fiber surface which consists primarily of basal plane exposures. Understanding the surface structure plays an important role in determining the approach to surface treating fibers.

CONCLUSIONS AND RECOMMENDATIONS

The structure of round cross-sectioned PAN-based fibers as they are presently fabricated (only a partial low-temperature oxidation) is circumferential on the outside and radial on the inside. The structure is the same for both intermediate and high-modulus type fibers. Complete low-temperature oxidation results in a completely circumferential structure.

In Rayon-based fibers, the crystallites near the outside of the fibers are oriented parallel to the fiber surface. In intermediate-modulus fibers, the center portion of the fibers is randomly oriented. In the high-modulus fibers, the orientation parallel to the fiber surface continues into the center of the fibers.

High resolution microscopy confirms that order exists in the fiber cross-section but further work is necessary to confirm whether the micro orientation is the same as the macro orientation, therefore, it is recommended that future work be aimed at the micro orientation of the cross-section (the orientation of the larger planes themselves) and the relationship between the micro and macro order. In relation to the fiber surface, the micro order at the surface also needs to be investigated. Finally, the relationship of defects and voids (where they occur and why) in the micro and macro structure needs further investigation.

FIGURE 10a. AREA A OF A HIGH-MODULUS PAN-BASED FIBER 1,100,000 X

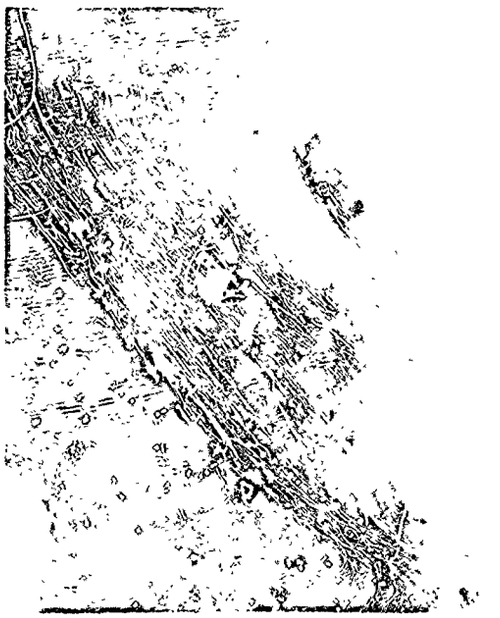


FIGURE 10b. AREA B OF A HIGH-MODULUS PAN-BASED FIBER 1,100,000X

FIGURE 10c. AREA NEAR SURFACE OF THORNEL 75 FIBER 1,000,000 X

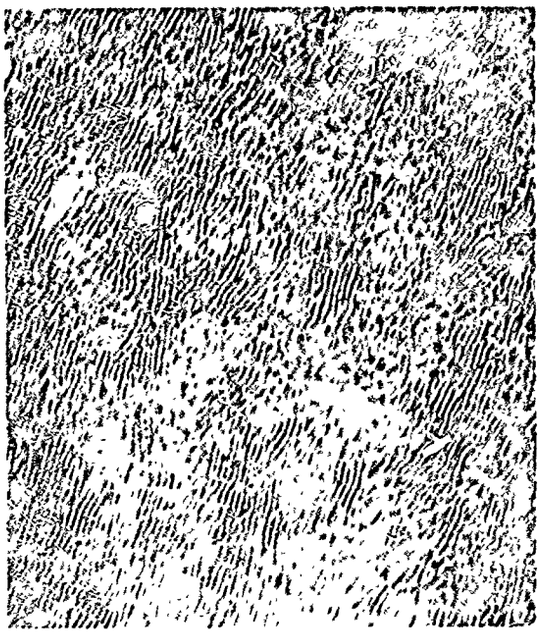


FIGURE 10d. AREA A OF AN INTERMEDIATE MODULUS PAN-BASED FIBER 2,500,000 X

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REFERENCES

1. Aitken, I. D., Rhodes, G., and Spencer, R. A. P., "Development of a Wet Oxidation Process for the Surface Treatment of Carbon Fiber", 3rd Conference on Industrial Carbons and Graphite, London: SCI, (1970).

2. Araki, T., and Comi, S., "Production of Molten Pitch Carbon Fiber", American Chemical Society Polymer Preprints, 9, 1388 (1968).

3. ASTM D-20, Subcommittee XVLLL, Sect. K and D-30, Subcommittee IV and V, "Proposed Method of Test for Tensile Properties of Strands, Yarns and Rovings", (1969).

4. Augl, J. M. and Wrasidlo, W. J., "Phenylated Polyquinoxalines from bis(phenyl-glyoxaoyl) Benzene", Journal of Polymer Science, A-1, 7, p 339, (1969).

5. Bacon, R., "Growth Structure and Properties of Graphite Whiskers", Journal of Applied Physics, 31, pp. 283-290, (1960).

6. Bacon, R., and Tang, M. M., "Carbonization of Cellulose Fibers-II. Physical Properties Study", Carbon, 2, pp. 221-225, (1964).

7. Bacon, R. and Schalamon, W. A., "Physical Properties of High-Modulus Graphite Fibers Made from a Rayon Precursor", American Chemical Society Polymer Preprints, 9, 1338 (1968).

8. Badami, D. V., Joiner, J. C. and Jones, G. A., "Microstructures of High Strength, High-Modulus Carbon Fibers", Nature, 215, pp. 386-387, (1967).

9. Bailey, J. E. and Clarke, A. J., "Carbon Fibers", Chemistry in Britain, 6, No. 11, pp. 484-489, (1970).

10. Bobka, R. J. and Lowell, L. P., "Integrated Research on Carbon Composite Materials", AFAPL-TR-310, Pt. I, (1966).

11. Brooks, C. S. and Scola, D. A., "An Examination of the Surface Reactivity of Graphite Fibers by Gas Chromatography", Journal of Colloid and Interface Science, 32, No. 4, (1970).

12. Brunauer, S., Emmett, P. H. and Teller, E., "Adsorption of Gases in Multimolecular Layers", Journal of the American Chemical Society, 60, pp. 309-318, (1938).

13. Butler, B. L., "The Effects of Carbon Fiber Microstructure on the Shear Strength of Carbon-Epoxy Composites", Ph. D. Thesis, Rensselaer Polytechnic Institute, (1969).

14. Central Scientific Company, "Surface and Interfacial Tensions by the Ring Method", Bulletin 101, Chicago, (1935).

15. Chemical Engineering News, 43, p. 23 (Nov. 1965).

16. Chwastiak, S., Union Carbide Corporation, private communication.

17. Chwastiak, S., "Wetting of Carbon Yarns from Wicking Rate Measurements", American Chemical Society Polymer Preprints, 31, No. 1, pp. 437-442, (1971).

18. Didchenko, R., "Carbon and Graphite Surface Properties Relevant to Fiber Reinforced Composites", AFML TR-68-45, (1968).

19. Ezekial, H. M. and Spain, R. G., "Preparation of Graphite Fibers from Polymeric Fibers", Journal of Polymer Science: PT. C, No. 19, pp. 249-265, (1967).

20. Ezekiel, H. M., "The Direct Graphitization of Polymer Yarns", American Chemical Society Polymer Preprints, 31, No. 1, pp. 415-425, (1971).

21. Ezekiel, H. M., "High Strength, High-Modulus Graphite Fibers", AFML TR-70-100, (1971).

22. Fiedler, A. K., Fitzer, E. and Muller, P. J., "Cyclization of Polyacrylonitrile as a First Step for Carbon Fiber Fabrication", American Chemical Society Polymer Preprints, 31, No. 1, pp. 380-387, (1971).

23. Fourdeux, A., Perret, R. and Roland, W., "General Structural Features of Carbon Fibers, Their Composites and Applications", London, pp. 9/1 - 9/10, (1971).

24. Goan, J. C., "Graphite Fiber Oxidation", NOLTR-69-153, (1969).

25. Goan, J. C. and Prosen, S. P., "Interfacial Bonding in Graphite Fiber-Resin Composites", Interfaces and Composites, ASTP 452, American Society for Testing and Materials, pp. 3-26, (1969).

26. Harling, D. F., "High Resolution Microscopy of Carbon Fibers", Proc. 28th Annual Electron Microscopy Society of America, Houston pp. 468-469, (1970).

27. Harling, D. F., "High Resolution Microscopy of Carbon Fibers", JOEL News, 9e, No. 2, pp. 22-26, (1971).

28. Herrick, J. W., "Surface Treatments for Fibrous Carbon Reinforcements", AFML TR-66-178, Pt. II, (1967).

29. Johnson, W. and Watt, W., "Structure of High-Modulus Carbon Fibers", Nature 215, pp. 384-386, (1967).

30. Johnson, J. W., Marjoram, J. R. and Rose, P. G., "Stress Graphitization of Polyacrylonitrile Based Carbon Fibers", Nature, 221, p. 357, (1969).

31. Johnson, D. J., "The Microstructure of Various Carbon Fibers", International Conference on Carbon Fibers, Their Composites and Applications, London, pp. 8/1 - 8/5, (1971).

32. Kinna, M. A., "NOL Ring Test Methods", NOLTR 64-156, (1964).

33. Knibbs, R. K., AERE, Harwell, private communication.

34. Kraus, E. H., Hunt, W. F. and Ramsdell, L. S., Minerology, McGraw Hill, Inc., New York, (1951).

35. Larsen, J. V., "The Scanning Electron Microscope and Its Applications in Fracture Studies of Composite Materials", NOLTR 69-189, (1969).

36. Liberman, M. L., "The Chemistry of Sulfur in Rayon-Based Carbon Fibers", American Chemical Society Polymer Preprints, 31, No. 1, pp. 370-379, (1971).

37. Lin, R. Y. and Economy, J., "Crystallite Orientation in Glassy Carbon Fibers", American Chemical Society Polymer Preprints, 31, No. 1, pp. 403-405, (1971).

38. Mantell, C. L., Carbon and Graphite Handbook, Interscience Publishers, New York, (1968).

39. McCreight, L. R., Rauch, H. W. and Sutton, W. H., Ceramic and Graphite Fibers and Whiskers, Academic Press, New York, (1965).

40. Mimeault, V. J. and McKee, D. W., "Surface Areas of Carbon Fibers", Nature, 224, pp. 793-794, (1969).

41. Mimeault, V. J., "Carbon Fiber Composites", American Chemical Society Polymer Preprints, 31, No. 1, pp. 479-487, (1971).

42. Moreton, R., Watt, W. and Johnson, W., "Carbon Fibers of High Strength and High Breaking Strain", Nature, 213, p. 690, (1967).

43. Norr, M. K., NOL, unpublished results.

44. Pease, E. C., Histological Techniques for Electron Microscopy, Academic Press, New York, (1964).

45. Quackenbush, N. E. and Thomas, R. L., "Investigation of Carbon Filament Reinforced Plastics", Aeroneutronic Publication No. U-4065, (1967).

46. Scola, D. A. and Brooks, C. S., "Investigation and Chemical Nature of the Surface of Recently Developed Fibers", AFML TR-67-218, Pt. II, (1968).

47. Scola, D. A. and Brooks, C. S., "Surface Aspects of New Fibers, Boron, Silicon Carbide and Graphite", Journal of Adhesion, 2, pp. 213-237, (1970).

48. Shaver, R. G., "Silicon-Carbide Whiskered Graphite Fibers", AICHE Materials Conference, Phila., (1968).

49. Shindo, A., "Studies on Graphite Fiber", Journal of the Ceramic Society of Japan, 69, c 195, (1961); Report No. 317 of the Government Industrial Research Institute, Osaka, (1961).

50. Shindo, A. and Soma, I., "The Carbonization of Polyvinyl Alcohol Fiber", Preprints of the Carbon Conference, Tokyo, (1964).

51. Simon, R. A., Prosen, S. and Duffy, J., "Carbon Fiber Composites", Nature, 213, pp. 1113-1114, (1967).

52. Standage, A. E. and Prescott, R., "High Elastic Modulus Carbon Fiber", Nature, 211, p. 139, (1966).

53. Steingiser, S. and Cass, R. A., "Graphite Fiber Reinforced Composites", AFML TR-68-357, Pt. II, (1970).

54. Tang, M. M. and Bacon, R., "Carbonization of Cellulose Fibers-I. Low Temperature Pyrolysis", Carbon, 2, pp. 211-220, (1964).

55. Tuinstra, F., and Koenig, J. L., "Raman Spectrum of Graphite", Journal of Chemical Physics, 53, No. 3, pp. 1125-1129, (1970).

56. Tuinstra, F. and Koenig, J. L., "Characterization of Graphite Fiber Surfaces with Raman Spectroscopy" Journal of Composite Materials, 4, pp. 492-499, (1970).

57. Watt, W., Phillips, L. N. and Johnson, W., "High-Modulus, High Strength Carbon Fibers", The Engineer, 221, p. 815, (1966).

58. Watt, W. and Johnson, W., "The Effect of Length Changes During Oxidation of Polyacrylonitrile Fibers on the Young's Modulus of Carbon Fibers", American Chemical Society Polymer Preprints, 9, No. 2, pp. 1245-1255, (1968).

59. Watt, W. and Green, J., "The Pyrolysis of Polyacrylonitrile", International Conference on Carbon Fibers, Their Composites and Applications, London, pp. 4/1 - 4/9, (1971).

60. Watt, W., private communication.

61. Winchell, A. N., Elements of Optical Minerology, John Wiley, New York, (1937).

62. Yamamoto, M., et al, "Determination of Wettability of High-Modulus Carbon Fiber by Its Matrix Resin", International Conference on Carbon Fibers, Their Composites and Applications, London, pp. 21/1 - 21/5, (1971).

63. Zisman, W. A., "Surface Chemistry of Plastics Reinforced by Strong Fibers", NRL Report 6911, (1969).